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Mixing dynamics and microscopic correlation of associated liquids

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Abstract : In the present work we outline the role of time-dependent probability theory in explaining the mixing dynamics of two liquids, as an extension of work carried out by D Bertolini *et al* (1998) [1] Exact form of microscopic correlation function and its relation to molecular structure and interaction are proposed

Keywords : Dielectric relaxation, Debye behaviour associating liquids, dipole correlation function

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1. Introduction

The process of dielectric relaxation, particularly in solution, is a very complex and interesting topic of scientific discussion, in the sense that an in-depth understanding of the subject is not complete. A novel approach in this regard was the work carried out by D Bertolini *et al* (1998) [1], in which, they have developed a dielectric relaxation model as a set of first order differential equations in some very generally conceivable parameters. Dielectric relaxation model has been developed for two associated liquids, by writing differential equations for dipole correlation function, and herein lies the beauty of the approach.

In this paper we have further interpreted the parameters in the aforesaid relaxation model, as probabilities, and also predict the forms of dipole correlation functions. At first, a basic introductory understanding of the relaxation model is presented. Then, we have found the interpretation for the microscopic correlation function. In the last section of this paper, we interprete the parameters in the aforesaid relaxation model, as probabilities. Then in the same section, we write the explicit

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functional forms of microscopic correlation functions. The section concludes two axioms proposed by us regarding the properties of the dipole correlations.

2. Dielectric relaxation model

Assumptions :

Let us first assume that that the dynamics of mixing of two liquids can be described by introducing some very general dynamical parameters, which take into account the short-range interactions occurring in the solution. These parameters, together with the relaxation rates of these molecules, then, will affect the relaxation process.

In lieu of explicitly adding diffusion terms in the equations, and then directly developing the dielectric relaxation model, the effect is included by developing the relaxation model from mixing dynamics of the liquids. Owing to diffusional processes the existing molecular environments in a binary solution will be continuously formed and destroyed. In this case the mixing dynamics can be described by a set of differential equations, from which we tend to develop the relaxation model afterwards

The dynamics of mixing :

Inside a binary solution at constant temperature, three different types of microscopic dynamically environment coexist, in each of which different types of short range interactions will be dominant : These three systems are individual molecules of the two liquids separately, and the molecules of both the liquids. Owing to diffusional processes, these environments will be continuously formed and destroyed. In this case the mixing dynamics can be described by the following set of differential equations (1),

$$\begin{aligned}
\dot{r}_1(x_1,t) &= \frac{b_{12}}{2} r_1(x_1,t)\, r_2(x_1,t) + \frac{a_{12}}{2} p_{12}(x_1,t) \\
\dot{p}_{12}(x_1,t) &= b_{12} r_1(x_1,t)\, r_2(x_1,t) - a_{12} p_{12}(x_1,t) \\
\dot{r}_2(x_1,t) &= -\frac{b_{12}}{2} r_1(x_1,t)\, r_2(x_1,t) + \frac{a_{12}}{2} p_{12}(x_1,t)
\end{aligned} \tag{1}$$

These equation shows that mixing of two liquids is a nonlinear process, and this peculiarity will lead to some difficulties, while discussing relaxation phenomena.

Here r_1 and r_2 are the fractions of molecules that at the time t belong to environments of first and second types respectively. While p_{12} is the fraction of molecules which are found in the mixed environments. x_1 is the molar fraction of liquid 1; a_{12} is the escaping rate of a tagged molecule from the environment (Breaking rate) while b_{12} is its entering rate (forming rate). It is important to underline the basic difference between these parameters. The breaking rate a_{12} is related to short range interactions while the forming rate b_{12} will depend also on the diffusional processes and could be in principle, a fraction of molar concentration since the number of

molecules is conserved, and we must have

$$\begin{aligned} r_1(x_1,t)+\frac{p_{12}(x_1,t)}{2} &= x_1 \\ r_2(x_1,t)+\frac{p_{12}(x_1,t)}{2} &= 1-x_1. \end{aligned} \tag{2}$$

These two equations describe mixing dynamics using only two parameters, which depend on the molecular interaction (hydrogen bond, dipolar interactions *etc.*) occurring in the solution.

For solution, of these equations, let,

$$r_1(x_1,0)=x_1 \quad \text{and} \quad r_2(x_1,0)=1-x_1.$$

Eq. (1) can be expanded around the equilibrium solution; neglecting non-linear terms and using (2) we get,

$$\begin{aligned} \delta\dot{r}_1(x_1,t) &= -\frac{b_{12}}{2}\left[\bar{r}_1(x_1)\delta r_2(x_1,t)+\bar{r}_2(x_1)\delta r_1(x_1,t)\right]+\frac{a_{12}}{2}\delta p_{12}(x_1,t) \\ \delta\dot{p}_{12}(x_1,t) &= b_{12}\left[\bar{r}_1(x_1)\delta r_2(x_1,t)+\bar{r}_2(x_1)\delta r_1(x_1,t)\right]-a_{12}\delta p_{12}(x_1,t) \\ \delta\dot{r}_2(x_1,t) &= -\frac{b_{12}}{2}\left[\bar{r}_1(x_1)\delta r_2(x_1,t)+\bar{r}_2(x_1)\delta r_1(x_1,t)\right]+\frac{a_{12}}{2}\delta p_{12}(x_1,t). \end{aligned} \tag{3}$$

From eq. (3) we can show that the fluctuatuations $\delta r_1(x_1,t)$, $\delta r_2(x_1,t)$ and $\delta p_{12}(x_1,t)$ decay exponentially with a rate $b_{12}\sqrt{\Delta/2}$, where

$$\Delta = 1+\frac{2a_{12}}{} - 4x_1(1-x_1)$$

This decay rate is just the inverse of mixing time.

The dielectric relaxation model :

For a liquid mixture in its equilibrium condition, r_1, r_2 and p_{12} fluctuate around their equilibrium values according to eq. (3). Accepting the presence of three processes, the dielectric relaxation model can be developed by writing three equations (similar to eq. (1)) for dipole correlation function (DCF). In setting up these equations, it is important to notice that the DCF is only affected only when a molecule goes into the mixed state. If we denote with $\varphi_1(x_1,t)$, $\varphi_2(x_1,t)$, $\varphi_{12}(x_1,t)$, the normalized dipole correlation functions in the three different environments, we obtain

$$\dot{\varphi}_1(x_1,t) = -\ k_1 + \frac{b_{12}}{2}\bar{r}_2(x_1)\ \varphi_1(x_1,t) + \frac{a_{12}}{2}\varphi_{12}(x_1,t)$$

$$\dot{\varphi}_{12}(x_1,t) = -(a_{12}+k_{12})\varphi_{12}(x_1,t) + \frac{b_{12}}{2}\left[\bar{r}_2(x_1)\varphi_1(x_1,t) + \bar{r}_1(x_1)\varphi_2(x_1,t)\right] \quad (4)$$

$$\dot{\varphi}_2(x_1,t) = -\ k_1 + \frac{b_{12}}{2}\bar{r}_2(x_1)\ \varphi_2(x_1,t) + \frac{a_{12}}{2}\varphi_{12}(x_1,t)$$

Here k_1, k_2, k_{12} are the relaxation rates in the respective environments, their values will be assumed by supposing that the rotational diffusion essentially depends on the interactions among the nearest molecules.

The arguments reported here refer to the mixing of two liquids, which show no characteristic association in their pure state. We will consider the association of two associated liquids in the following sections.

Two associated liquids :

When a mixture is made up of two liquids which in their pure state are structured (*e.g.* by hydrogen bond) the eqs. (1) must be generalized in order to take into account also the structural dynamics in the two environments 1 and 2 respectively where interactions among molecules of same type are dominant. So let p_1, r_1 and p_2, r_2 be the structured and non structured fractions inside environment 1 and 2 respectively The breaking and forming rates inside these environments are denoted by a_1, b_1 and a_2, b_2 respectively.

The equations describing the dielectric relaxation are

$$\dot{\varphi}_1(x_1,t) = -\ a_1 + \frac{b_{12}}{2}\left[\bar{r}_2(x_1) + \bar{p}_2(x_1)\right] + k_1\ \varphi_1(x_1,t) + b_1\chi_1(x_1,t) + \frac{a_{12}}{4}\varphi_{12}(x_1,t)$$

$$\dot{\chi}_1(x_1,t) = -\ b_1 + \frac{b_{12}}{2}\left[\bar{r}_2(x_1) + \bar{p}_2(x_1)\right] + \gamma_1\ \chi_1(x_1,t) + a_1\varphi_1(x_1,t) + \frac{a_{12}}{4}\varphi_{12}(x_1,t)$$

$$\dot{\varphi}_{12}(x_1,t) = -(a_{12}+k_{12})\varphi_{12}(x_1,t) + \frac{b_{12}}{2}\left[\bar{r}_2(x_1) + \bar{p}_2(x_1)\right]$$

$$x\left[\chi_1(x_1,t) + \varphi_1(x_1,t)\right] + \left[\bar{r}_1(x_1) + \bar{p}_1(x_1)\right] x\left[\chi_2(x_1,t) + \varphi_2(x_1,t)\right] \quad (5)$$

$$\dot{\varphi}_2(x_1,t) = -\ a_2 + \frac{b_{12}}{2}\left[\bar{r}_1(x_1) + \bar{p}_1(x_1)\right] + k_2\ \varphi_2(x_1,t) + b_2\chi_2(x_1,t) + \frac{a_{12}}{4}\varphi_{12}(x_1,t)$$

$$\dot{\chi}_2(x_1,t) = -\ b_2 + \frac{b_{12}}{2}\left[\bar{r}_1(x_1) + \bar{p}_1(x_1)\right] + \gamma_2\Big|\chi_2(x_1,t) + a_2\varphi_2(x_1,t) + \frac{a_{12}}{4}\varphi_{12}(x_1,t).$$

In eq. (5) the parameters, k_1, γ_1, k_{12}, γ_2 and k_2 are the orientation rates of the molecules having dielectric correlation function equal to φ_1, χ_1, φ_{12}, χ_2 and φ_2 respectively. But it is important to remark that when $p_1 >> r_1$ and $p_2 >> r_2$, eq. (5) coincides with eq. (1), so also the corresponding dielectirc behaviour.

3. An interpretation of dielectric correlation function (DCF)

As has been pointed out in the beginning, the dielectric relaxation model has been developed for two associated liquids, by writing differential equations for dipole correlation functions. So, it will Be noteworthy to find some physical interpretation for the DCFs at this point.

If [2]

$$M^0 = \sum^{\cdot\cdot} \mu_i \tag{6}$$

is the contribution of the permanent moments to the total moment M. An autocorrelation function for M_0 is defined as

$$\varphi^{or}_{sph}(t) = \frac{\langle M^0(0) \cdot M^0(t) \rangle}{\langle M^0 \cdot M^0 \rangle} \tag{7}$$

Also the microscopic correlation functions

$$\gamma(t) = \frac{\langle \mu(0)_i \cdot M_1(t) \rangle}{\langle \mu(0)_i \cdot M_1(t) \rangle} \quad \frac{\left\langle \mu_i(0) \cdot \sum^{\cdot} \mu_j(t) \right\rangle}{\left\langle \mu_i(0) \cdot \sum_{j=1}^{N} \mu_j(0) \right\rangle} \tag{8}$$

Where, $M_1(t) \cdot \sum^{\cdot\cdot}_{j=1} \mu_j(t)$ denotes the sum of the permanent moments in a sphere that is small with respect to the dielectric so that its average value is fixed. The relation of mis MCF to the time dependent generalization $g(t)$ of Kirkwood correlation function g is

$$g(t) = g\gamma(t) = \frac{1}{\mu^2} \langle \mu(0), M_j(t) \rangle = \frac{1}{\mu^2} \left\langle \mu_i(0) \cdot \sum_{j=1}^{N} \mu_j(t) \right\rangle \tag{9}$$

The relation between $\varphi^{or}_{sph}(t)$ and complex permittivity is

$$\frac{\hat{\varepsilon}(\omega) - \varepsilon_\infty}{\hat{\varepsilon}(\omega) + 2} = \frac{\varepsilon - \varepsilon_\infty}{\varepsilon + 2} \left[1 - i\omega L\left(\varphi^{or}_{sph}(t)\right) \right] \tag{10}$$

For a liquid the function $\varphi^{or}_{sph}(t)$ differs from a microscopic correlation function, since it incorporates the long-range dipole-dipole interaction in the polar liquid The dipole correlation functions implied in eq (4) are obviously the microscopic correlation functions The Laplace transform of $\gamma(t)$ is related to the complex permittivity as

$$\frac{(\hat{\varepsilon}(\omega)-\varepsilon_\infty)(2\hat{\varepsilon}(\omega)+\varepsilon_\infty)\varepsilon}{\hat{\varepsilon}(\omega)-\varepsilon_\infty)(2\varepsilon+\varepsilon_\infty)} = 1-i\omega L\{\gamma(t)\} \tag{11}$$

4. Proposals

Probabilistic interpretation

It appears to us that r_1 and r_2 will be the probabilities that at the time t a particular molecule belong to environments of first and second types respectively While p_{12} is the probability that a molecule of type 1 or 2 will be found in the mixed environments The probabilities r_1, r_2 and p_{12} are time dependent x_1 is the probability that a molecule chosen at random from the sample is of type 1, irrespective of the environment from which it has been chosen Obviously x_1 does not depend on time a_{12}, ∂T is the probability that a particular bond wall be broken in time ∂T, while $b_{12}\partial T$ is the probability that a particular bond will be formed in time ∂T With such probabilistic interpretation, which depends on time, we argue that the dynamics can be interpreted as a stochastic process

Forms of microscopic correlation functions (MCF)

In view of eq (8), we define the functions φ_1, λ_1, φ_{12}, λ_2 and φ_2 as

$$b_1(t) = \frac{\left\langle \mu_{Ai}(0) \sum_{j=1}^{N} \mu_{jA}(t) \right\rangle}{\left\langle \mu_{iA}(0) \sum_{j=1}^{N} \mu_{Aj}(0) \right\rangle} \tag{12a}$$

$$\chi_1(t) = \frac{\left\langle \mu_{Ai}(0) \sum_{j=1}^{N} \mu_{jB}(t) \right\rangle}{\left\langle \mu_{iA}(0) \sum_{j=1}^{N} \mu_{Bj}(0) \right\rangle} \tag{12b}$$

$$\phi_{21}(t) = \frac{\left\langle \mu_{BAi}(0) \sum_{j=1}^{N} \mu_{jBA}(t) \right\rangle}{\left\langle \mu_{iAB}(0) \sum_{j=1}^{N} \mu_{ABj}(0) \right\rangle} \tag{12c}$$

$$\lambda_2(t) = \frac{\left\langle \mu_{Bi}(0) \sum_{j=1}^{N} \mu_{jA}(t) \right\rangle}{\left\langle \mu_{iB}(0) \sum_{j=1}^{N} \mu_{jA}(0) \right\rangle} \tag{12d}$$

$$\varphi_2(t) = \frac{\left\langle \mu_{Bi}(0) \sum_{j=1}^{N} \mu_{Bj}(t) \right\rangle}{\left\langle \mu_{iB}(0) \sum_{j=1}^{N} \mu_{Bj}(0) \right\rangle} \tag{12e}$$

Properties of dipole correlation in liquid

Although, our final aim is to obtain the solutions of coupled differential equation of first order eq (5), for which some amount of simplifications will be necessary But due to empirical nature of the model, it is not possible for us, at this point, to make reasonably good assumptions, So, let us first form following axioms regarding the properties of the dipole correlations before actually solving the equations

Proposal 1 Functional form of microscopic correlation function is independent of molecular structure of a liquid

Proposal 2 Functional form of microscopic correlation function only depends upon only the type of interaction prevailing among different types of molecules

The logic behind these proposals are at once clear if we note that the 1st, the 2nd, the 4th and the 5th equation of eq (5) are similar in form while the third one is different Therefore the solutions of the 1st, the 2nd, the 4th and the 5th equation of eq (5) should be similar in form, but the third of these equations should have a solution which is different in form

5 Conclusion

The mixing dynamics, and hence the process of dielectric relaxation in a diffusion dominated environment is established as a stochastic process Regarding the form of MCF, we noted that it is independent of molecular structure of a liquid, but only depends upon only the type of interaction prevailing among different types of molecules

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